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FACTORS AFFECTING SULFATE RESISTANCE OF MORTARS.(U)

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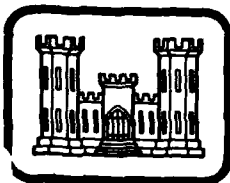
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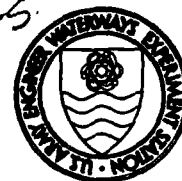
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# FACTORS AFFECTING SULFATE RESISTANCE OF MORTARS

by

Katharine Mather

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20. ABSTRACT (continued).

I - III

Cements investigated included portland cements of Types I, II, III, and V meeting ASTM C 150; blended cements including Type IP's meeting ASTM C 595 that were made from the same clinkers as the Type I's; and Type I's blended with pozzolans including fly ashes produced by burning bituminous, subbituminous, and lignitic coals, calcined natural volcanic glass high in silica, and silica fume. Silica fume forms glassy microspheres that may contain over 90% percent  $\text{SiO}_2$ ; it is a by-product of the production of silicon metal.

Some of the fly ashes produced from subbituminous and lignitic coals replacing 30% percent by volume of cements increased the expansion of mortars containing the blends when stored in sulfate solutions. This behavior reflects  $\text{SiO}_2$  below 50% percent,  $\text{Al}_2\text{O}_3$  16 to 26% percent, and  $\text{CaO}$  5 to 30% percent. Other investigations show that  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  in the fly ash glass are readily available to combine with sulfate to form ettringite. With cement of lower  $\text{C}_3\text{A}$  content, some of the subbituminous and lignitic fly ash blends improved the sulfate resistance of mortars, except when  $\text{SiO}_2$  in the fly ashes was 38% percent or less. ✓

Type IP blended cements made with portland-cement clinkers containing up to 11 percent calculated  $\text{C}_3\text{A}$  and about 20 percent fly ash show substantial improvement in sulfate resistance of mortars compared with Type I cements made from the same clinkers.

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## PREFACE

The research cited in this paper is part of the Corps of Engineers Civil Works Research Program Work Unit 31295, "Substitutes for Sulfate-Resistant Cement."

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The research was conducted and the paper prepared under the general supervision of Bryant Mather, Chief, Structures Laboratory.

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# FACTORS AFFECTING SULFATE RESISTANCE OF MORTARS<sup>(1)</sup>

by

Katharine Mather<sup>(2)</sup>

## SUMMARY

The ability of a mortar made using portland cement, fine aggregate, and water to resist attack by sulfates is affected by the proportions of the mortar (water-cement ratio and cement content), by the maturity, by the amount of tricalcium aluminate in the portland cement, by the presence of tricalcium aluminate-sodium oxide solid solutions with different structures and reactivities, and by the composition, reactivity, and amount of pozzolan used together with the portland cement.

Cements investigated included portland cements of Types I, II, III, and V meeting ASTM C 150, blended cements including Type IP's meeting ASTM C 595 that were made from the same clinkers as the Type I's, and Type I's blended with pozzolans including fly ashes produced by burning bituminous, subbituminous, and lignitic coals, calcined natural volcanic glass high in silica, and silica fume. Silica fume forms glassy microspheres that may contain over 90 percent  $\text{SiO}_2$ ; it is a by-product of the production of silicon metal.

Some of the fly ashes produced from subbituminous and lignitic coals replacing 30 percent by volume of cements increased the expansion of mortars containing the blends when stored in sulfate solutions. This behavior reflects  $\text{SiO}_2$  below 50 percent,  $\text{Al}_2\text{O}_3$  16 to 26 percent, and  $\text{CaO}$  5 to 30 percent. Other investigations show that  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  in the fly

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(1) Prepared for Seminar at Seventh International Congress on the Chemistry of Cement, Paris, France, 30 June 1980.

(2) Special Technical Assistant, Structures Laboratory, U. S. Army Engineer Waterways Experiment Station, Vicksburg, Miss. 39180, USA.

ash glass are readily available to combine with sulfate to form ettringite. With cement of lower  $C_3A$  content, some of the subbituminous and lignitic fly ash blends improved the sulfate resistance of mortars, except when  $SiO_2$  in the fly ashes was 38 percent or less.

Type IP blended cements made with portland-cement clinkers containing up to 11 percent calculated  $C_3A$  and about 20 percent fly ash show substantial improvement in sulfate resistance of mortars compared with Type I cements made from the same clinkers.

RESUMÉ : La résistance au sulfate des mortiers est affectée par le rapport eau/ciment et la teneur en ciment (dont il n'est pas parlé) ainsi que par la quantité d'aluminate tricalcique dans le ciment portland, la présence des solutions solides du sodium dans l'aluminate tricalcique de diverses structures et réactivités et par la composition, la métastabilité thermique et la quantité de pouzzolane employée pour remplacer une partie du ciment portland dans le but d'augmenter la résistance au sulfate du mortier.

Les ciments hydrauliques étudiés comprenaient les Types I, II, III, et V répondant à la spécification ASTM C 150, les ciments de Type IP répondant à la spécification ASTM C 595 fabriqués à partir des mêmes clinkers que les ciments de Type I, et du Type I comportant de la pouzzolane, y compris les cendres volantes produites par la combustion de charbons bitumineux, subbitumineux et lignitiques, le verre volcanique naturel calciné à haute teneur en silice et les fumées de silice. Les fumées de silice forment des microsphères hyalines pouvant contenir plus de 90 pour cent de  $SiO_2$ ; elles sont un sous-produit de la production de métal au silicium.

Les cendres volantes produites par les charbons subbitumineux et lignitiques remplaçant 30 pour cent du volume des ciments à haute teneur en  $C_3A$  cubique augmentèrent l'expansion en sulfate de sodium des mortiers contenant les mélanges. Ce comportement représente  $SiO_2$  au-dessous de 50 pour cent,  $Al_2O_3$  de 16 à 26 pour cent et  $CaO$  de 5 à 30 pour cent. D'autres analyses indiquent que  $Al_2O_3$  et  $CaO$  présents dans le verre de cendre volante peuvent permettre la formation d'ettringite. Dans le cas des ciments à



plus faible teneur en  $C_3A$  cubique les mélanges de cendres volantes sub-bitumineuses et lignitiques améliorent la résistance au sulfate des mortiers, sauf lorsque la proportion de  $SiO_2$  dans les cendres est de 38 pour cent ou moins. Les effets de mélanges de  $C_3A$  cubique et orthorhombique I et de  $C_3A$  orthorhombiques ou tétragonaux seront également étudiés.

Les ciments mélangés du Type IP produits à partir de clinkers contenant jusqu'à 11 pour cent de  $C_3A$  calculé et environ 20 pour cent de cendres volantes démontrent une amélioration sensible dans la résistance au sulfate des mortiers par rapport aux Types I produits à partir des mêmes clinkers.

## INTRODUCTION

The chemical resistance of pastes, mortars, and concretes made using portland cement is affected by the proportions of the mixture (water-cement ratio and cement content), by the presence and amount of various solid solutions of  $C_3A$  with different structures and containing  $Na_2O$ ,  $K_2O$ ,  $SiO_2$ ,  $Fe_2O_3$ ,  $MgO$ , etc. If a pozzolan is used together with the portland cement, its composition, reactivity, and proportion in the mixture will affect for good or evil the sulfate resistance of the system.

## CEMENTITIOUS MATERIALS

In the work upon which this paper is based, the sulfate resistance of mortars containing portland cements complying with the requirements for Types I, II, III, and V of ASTM C 150-78, Standard Specification for Portland Cement, and also cements complying with the requirements for Types IP and IS of ASTM C 595, Standard Specifications for Blended Hydraulic Cements, was investigated. In most cases we were able to test the Type I and the Type IP and the Type I and Type IS sampled at the same time from the same plant. We also tested four bituminous fly ashes, three sub-bituminous fly ashes, four lignitic fly ashes, a calcined natural volcanic glass, a glassy silica fume of high silica content that is a waste product in the production of silicon metal, and a sample of Santorin earth. Some of the materials studied are not reported on here.

## MORTARS

The mortars were made with one part of cement to 2.75 parts graded standard sand to 0.485 parts of water, by weight. When other materials were used, the water content was changed until the flow of the mortar was equal to that of the mortar containing portland cement alone. Reductions were necessary with some of the portland-pozzolan cements; one pozzolan having very high surface area increased the water-cement ratio by about 3 percent.

## TEST SPECIMENS AND INITIAL TESTS

All the specimens cast were 25.4 mm by 25.4 mm by 285.8 mm long with gage studs at both ends. All were cured for 24 hr in sealed molds in water at  $35^{\circ} \pm 3^{\circ}\text{C}$ , then removed from the molds. The initial gage length,  $254 \pm 2.5$  mm, was determined; the fundamental transverse frequency was measured, and the bars were cured in water saturated with CH at a temperature of  $23^{\circ} \pm 1.7^{\circ}\text{C}$ . The same procedure was used for curing cubes of the same mortar which were broken in compression at various ages until the cubes reached the desired strength at which age the mortar bars were to be placed in 0.352-molar  $\text{Na}_2\text{SO}_4$  solution. Before the bars were placed in sulfate solution, the length and fundamental transverse frequency of each bar was again measured. The strengths at which the bars were placed in sulfate solution were equalized as well as possible so that cements compared in the test for sulfate-resistance would be at the same maturity as measured by compressive strength. The first tests were made with bars having a compressive strength of  $27.6 \pm 1.4$  MPa as measured in equivalent cubes; the next series at  $24.1 \pm 1.4$  MPa; the final choice of strengths was  $20.7 \pm 1.0$  MPa. The decision to lower the strength level was made because many portland, portland-pozzolan, and several portland blast-furnace slag cements survived the test for one year and did not fail by breaking although they expanded well over 1.0 percent of the gage length. There thus seems to be a wide variation in the strain capacity of mortar bars made with different portland, portland-pozzolan, and portland blast-furnace slag cements as well as among those made using blends of different

portland cements with 30 or 35 percent replacement of cement by absolute volume of pozzolan.

#### LATER TESTS

The bars were subsequently measured for length change and tested for fundamental transverse frequency at 7, 14, 21, 28, 56, and 90 days. Thereafter the schedule for measurements was adjusted to the rate at which the expansion was increasing and the relative dynamic modulus of each group of mortar bars was decreasing. Each time the bars were measured, the sulfate solution was changed and since the measurement interval was not constant throughout the test it was not to be expected that a constant amount of sulfate was available to attack the bars during each interval between readings. The volume of sulfate solution to bars was maintained at 3.9 to 1 throughout the test.

#### FAILURE CRITERIA

The criterion for failure by increase in length was chosen as 0.10 percent; some cements failed by having all of the mortar bars break at expansions which were not determined because the failure occurred between two readings and we only know for example that after an expansion of 0.44 percent at 28 days every bar was broken at 56 days, the time of the next reading. The earliest failures by fracture of any of the bars took place at 28 days. Failures by fracture occurred thereafter at ages up to 180 days, but there was a tendency among the portland cements for failures to occur at relatively low expansions at ages below 90 days or for failures to occur at markedly larger expansions where the bars would already have been judged to have failed simply on the basis of expansion.

#### TRICALCIUM ALUMINATE DETERMINATIONS

We investigated the form of  $C_3A$  or  $C_3A$  solid solution with sodium oxide, potassium oxide, magnesium oxide, or silicon dioxide (1) by X-ray diffraction using a diffractometer with nickel-filtered copper radiation; in all cases the portion of the cement examined had been treated with maleic acid in methanol solution stirred for 30 min and then filtered (2).

We have followed the method in Appendix A of Mander et al (2) except that we use as-received cement samples and stir for 30 min in the maleic acid-methanol solution, followed by vacuum filtration over a small piece of Nylon stocking under No. 50 Whatman filter paper in a Büchner funnel, three washes with methanol, and evaporation to free-flowing dryness under an infrared lamp. Sulfates are removed by a 10 percent solution of ammonium chloride in water, stirred at laboratory temperature with a magnetic stirrer for 45 min, filtered, and evaporated to free-flowing dryness as are the maleic-acid residues. Mander et al (2) and Regourd, Chromy, et al (4) provide X-ray diffraction spacings for cubic and orthorhombic  $C_3A$  and solid solutions of  $C_3A$  and sodium oxide. Regourd and Guinier (5) provide more information; we have assumed that Orthorhombique II mentioned by Regourd et al (4) is equivalent to "Monoclinic" in Regourd and Guinier (5) and Maki (6) except for the necessary differences in indexing. Like Kristmann (7) the diffractometer available to us resolved doublets in the relevant angular ranges of  $C_3A$  and solid solutions in  $C_3A$  but did not resolve triplets. Therefore, we used in our separations of  $C_3A$  the lines in the angular region from 21 to 21.84 degrees two-theta. As a consequence we believe that the separation of cubic  $C_3A$  from other  $C_3A$  is reliable as is the absence of  $C_3A$  from the maleic acid residue. The distinction of the cubic and orthorhombic or tetragonal  $C_3A$  from orthorhombic and tetragonal or orthorhombic or tetragonal we suspect may be less reliable.

#### EFFECTS OF TRICALCIUM ALUMINATE CONTENT

Initially let us consider cements in which no  $C_3A$  was detected by X-ray diffraction. Five such portland cements were found. Only one had been tested for one year and it had expanded only to 0.065 percent at that time. The other four cements in which no  $C_3A$  was detected have been tested to 180 days at which time one which contains 4.53 percent M by chemical analysis has expanded to 0.085 percent, although it may expand more than 0.10 percent at one year, the influence of the periclase content hydrating to  $Mg(OH)_2$  is believed to be the significant feature explaining the expansion of this cement. All of the other three cements

contain less possible periclase. Six cements were recognized as containing orthorhombic or tetragonal or orthorhombic and tetragonal  $C_3A$ . These include one which in one year reached an expansion of 2.88 percent in mortar bars.

The strain capacity (i.e., the increase in length without fracturing) of this particular cement was the largest shown by any of the portland cements tested. Another cement reached an expansion of 0.861 percent at 146 days but was not measurable at 180 days. Clearly, the strain capacity was substantial but well below that of the cement just discussed. Three other cements reached expansions over 0.10 percent by 180 days. One of those which exceeded 0.10 percent at 180 days contained 4.36 percent M by chemical analysis. The sixth cement which contains slightly over 2 percent M expanded to 0.057 percent at 180 days. The question of the strain capacity of the mortar bars of four of these cements has not yet been answered since all are still under test and none in the four sets has fractured. Cements containing cubic and orthorhombic or tetragonal  $C_3A$  or cubic  $C_3A$  and one of the other two forms in this group made up eight cements. Seven of those tested have failed by exceeding 0.10 percent expansion and three have failed in fracture, two at quite low expansions, and the others at expansions above 0.58 percent.

Seven portland cements contained only cubic  $C_3A$ . One of these reached an expansion of 1.77 percent at 365 days with no mortar bars broken. Another at 90 days had expanded to 0.61 percent with four mortar bars broken. Another has achieved the same expansion at 180 days without any failures by fracture. A fourth expanded to 0.29 percent at 90 days and was unreadable at 146 days. A fifth has expanded beyond 0.20 percent at 180 days without failures in fracture. Two other cements have not failed. One is expected to because although it contains the least cubic  $C_3A$  detected it also contains 3.63 percent M by chemical analysis and has expanded to 0.085 percent at 180 days. While we endeavored to find out which substances were present in the 26 portland cements tested, our tests so far suggest, but do not confirm, the opinions of Regourd and Chromy et al (4) that cubic  $C_3A$  is more active than the forms with denser packing. Certainly the amount of  $C_3A$  in the cement as ranked by X-ray diffraction

is not invariably correlated with maximum expansion, usually because the cements with the highest  $C_3A$  contents also are cements of quite rapid strength gain and low strain capacity, so that they may fail in 56 to 90 days by exceeding 0.10 percent expansion and by having all of the mortar bars fail in fracture.

#### BEHAVIOR OF PORTLAND-POZZOLAN CEMENTS

A comparison was made between  $C_3A$  and solid solutions of the several crystal forms ranked by relative amount and the companion IP cements made with the same portland cement clinker and an addition ranging from 15 to possibly 25 percent of fly ash in the cements containing the most cubic  $C_3A$ . In the group of portland cements containing the largest amounts of cubic  $C_3A$  and their companion IP cements, all of the portland cements failed by expanding from 0.289 percent at 90 days where all fractured, up to as much as 1.77 percent where the bars survived to one year but relative E had fallen to 57 percent. Only one of the three companion IP cements expanded as much as 0.10 percent. One reached one year with an expansion of 0.035; it was the companion of the portland cement that expanded 1.77 percent. The other two cements are still under test with no apparent relation between the expansion of their companion portlands and those of the IP's. In the group of cubic  $C_3A$  cements, one portland with a relatively low amount of  $C_3A$  has a companion IP. The portland had expanded 0.61 percent at 180 days while the IP expanded 0.6 percent at the same age. In the group containing cubic and either orthorhombic or tetragonal  $C_3A$  solid solution or both, two portland cements have in one case two companion IP cements, one made with fly ash and one experimental cement with bottom ash. The other portland cement had a companion portland blast-furnace slag cement. The portland with IP companions is still under test but has substantially exceeded the failure criterion of 0.10 percent expansion. The companion IP still under test at the same age as the portland has expanded 0.08 percent while the experimental cement with bottom ash has already expanded over 0.90 percent at the same age. The portland cement with the companion portland blast-furnace slag cement expanded over 1 percent and failed by cracking and warping

at 146 days with a relative E of 49 percent. The portland blast-furnace slag cement reached an expansion of 0.08 percent at 292 days and was terminated. Among cements containing relatively small amounts of cubic and orthorhombic or tetragonal  $C_3A$  or solid solutions one Type I cement survived to an age of one year at an expansion of 1.40 percent; the companion cement expanded 0.43 percent at one year. The second portland cement is still under test but has exceeded the failure criterion of 0.10 percent expansion. It had two companion IP cements with different amounts of fly ash in each. One has expanded 0.04 percent and the other 0.05 percent at the same age as the portland; all three are continuing in test. In cements containing orthorhombic or tetragonal solid solutions or both one cement containing an intermediate amount of total  $C_3A$  expanded to 2.9 percent at one year with a relative E of 64 percent at that time. Its companion IP expanded 0.11 percent at one year with a relative E of 150 percent. Within the same group of  $C_3A$  solid solutions one containing a relatively small amount of total  $C_3A$  expanded 0.10 percent at 280 days and is still in test. Its companion which has been in test for 180 days has expanded 0.05 percent. In the same group of  $C_3A$  solid solutions the cement containing the least total aluminate phase has expanded to 0.86 percent at 146 days and was thereafter unreadable. Its companion IP has expanded 0.14 percent and is still under test. Summarizing these results shows that out of a total of 12 portland cements with companion blended cements, almost all blended with fly ash, 11 of the blended cements had expansions substantially reduced from those of the portland cements but in one case the addition of fly ash increased the total expansion but prolonged the life of the blended cement mortar bars from 90 days when all of the portland cement bars had broken to 270 days and the blended cement is still under test. Thus we have a clear case for the utility of Type IP cements.

#### BEHAVIOR OF BLENDS WITH HIGH-SILICA POZZOLANS

Three cements: RC 756 with 14.6 percent  $C_3A$  as calculated from chemical composition, RC 714 with 13.1, and RC 744 with 9.4 were tested alone and with 30 percent replacement by solid volume of each of two high-silica pozzolans. The  $C_3A$  in 756 was indicated by X-ray diffraction to be

cubic, that in 714 and 744 to be cubic and orthorhombic. The high-silica pozzolans were AD 518, a calcined volcanic glass, and AD 536, a silica fume.

As shown on Fig. 1, the three cements tested alone behaved as follows: RC 714 showed 0.515 percent expansion at 56 days and all the bars disintegrated before the next test age; RC 756 showed 0.868 percent expansion at 90 days and all the bars disintegrated before the next test age; and bars made with RC 744 all survived to 365 days at which time the expansion was 0.808 percent after which the bars began to warp.

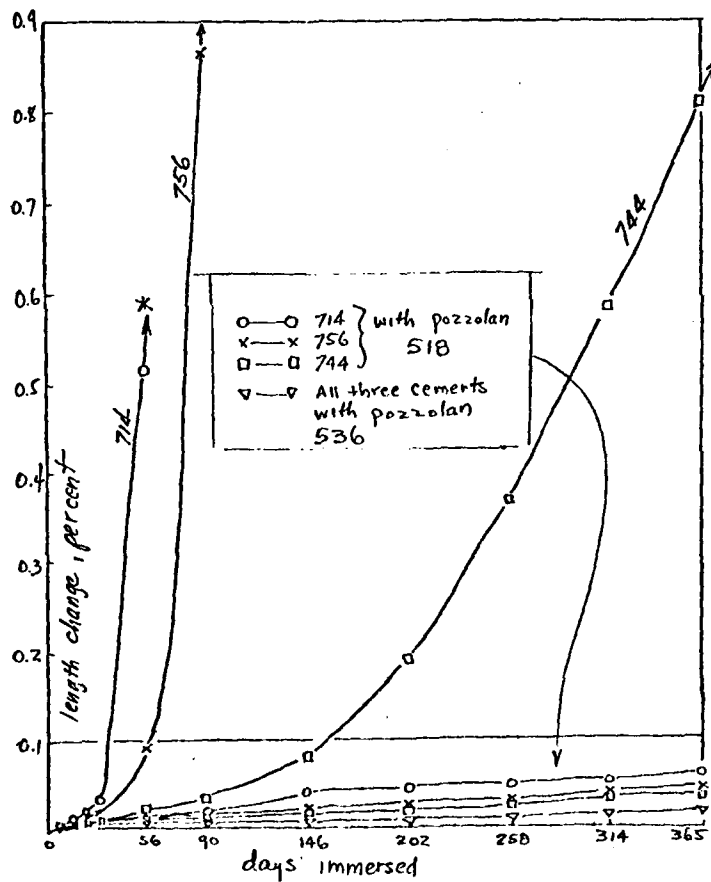


Figure 1



With 30 percent silica fume (AD 536) the expansions at 365 days with the three cements were insignificant and insignificantly different: 0.019, 0.016, and 0.018, respectively. With 30 percent calcined volcanic glass the expansions with the three cements remained in the order of expansion of the cements alone but were well below failure at one year being 0.057, 0.041, and 0.034, respectively. It is concluded that either of these two pozzolans at 30 percent replacement can effectively control sulfate expansion using any of these cements in this test; the silica fume is more effective and equally effective with all three cements. The volcanic glass still allows the cements to manifest their inherent differences in sulfate resistance but the expansion is at an innocuous level in all cases.

#### BEHAVIOR OF CEMENT 714 WITH FLY ASHES

Cement 714, by itself survived to 56 days, had expanded then 0.515 percent, and then disintegrated (Fig. 2).

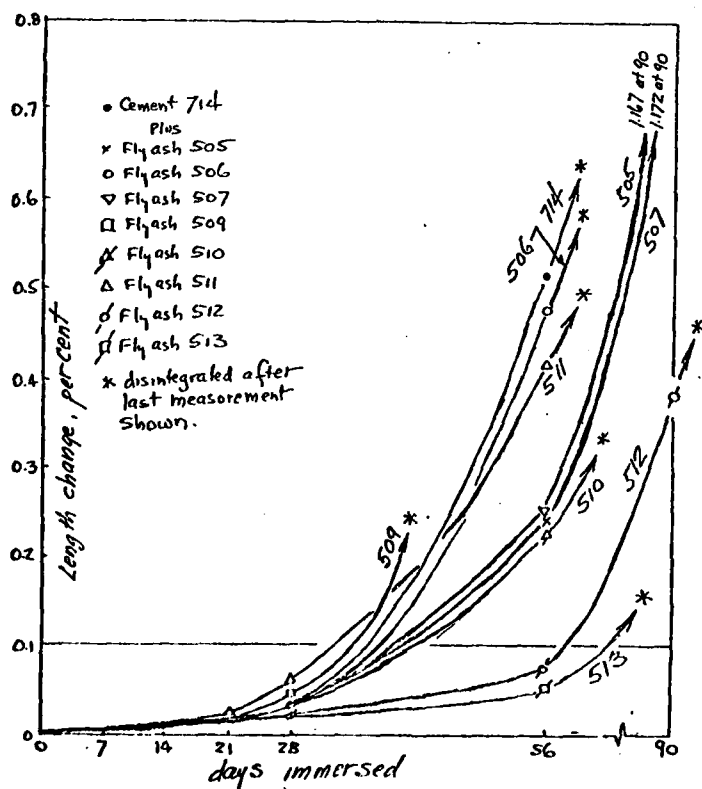


Figure 2

When replaced by 30 percent of each of eight fly ashes the effects varied. With fly ash 509 the specimens only survived 28 days after which they disintegrated, but at 28 days the expansion (0.040 percent) was less than when 511 was used. With fly ashes 506, 510, 511, and 513 the bars survived to 56 days but with widely different expansions at that point (0.427, 0.229, 0.417, and 0.056, respectively) and then disintegrated. With fly ashes 505, 507, and 512 the bars survived to 90 days, again with widely different expansions (1.167, 1.172, and 0.385, respectively). It is concluded that none of the eight fly ashes tested would control sulfate expansion of this cement in this test at 30 percent replacement. It is not positively shown however that any of the eight fly ashes made sulfate resistance significantly worse than it was when the cement was used alone.

#### BEHAVIOR OF CEMENT 756 WITH FLY ASHES

Cement 756, by itself survived to 90 days at which time its expansion was 0.867 (Fig. 3). When replaced by 30 percent of each of eight fly

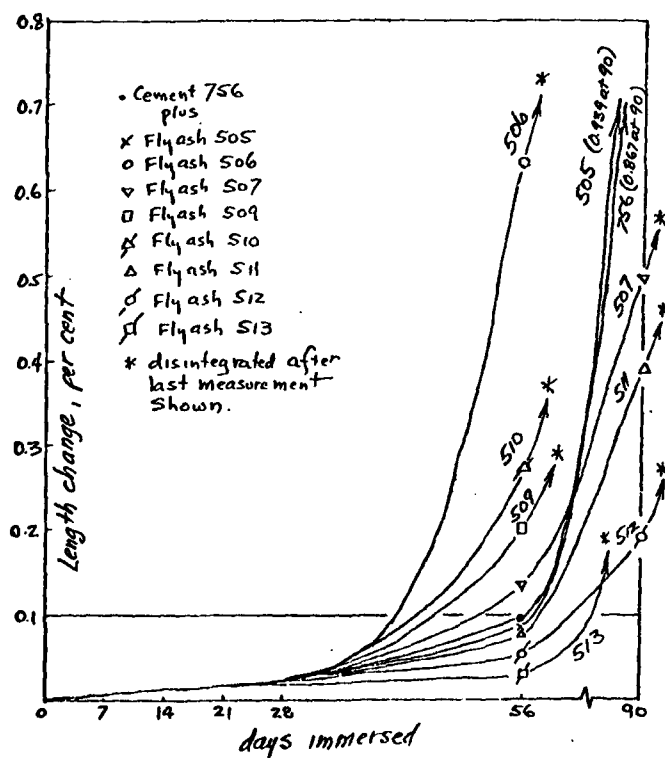


Figure 3

ashes, as was to be expected, the effects varied. Five of the fly ashes had an adverse effect on sulfate resistance. In four cases the specimens only survived 56 days at which time their expansions were:

506: 0.634	510: 0.276
509: 0.209	513: 0.031

In the fifth case, with 505, the bars survived to 90 days but with higher expansion (0.939) than the cement by itself. In the other three cases the bars survived as long as the cement by itself, but no longer, and had lesser but still large expansions (0.199, 0.392, and 0.500). It is concluded that none of these fly ashes will control sulfate expansion of this cement in this test at 30 percent replacement; five of the eight actually make the system less sulfate resistant.

#### BEHAVIOR OF CEMENT 744 WITH FLY ASHES

Cement 744, by itself survived to 365 days (Fig. 4), at which time its expansion was 0.808 percent. When replaced by 30 percent of each of

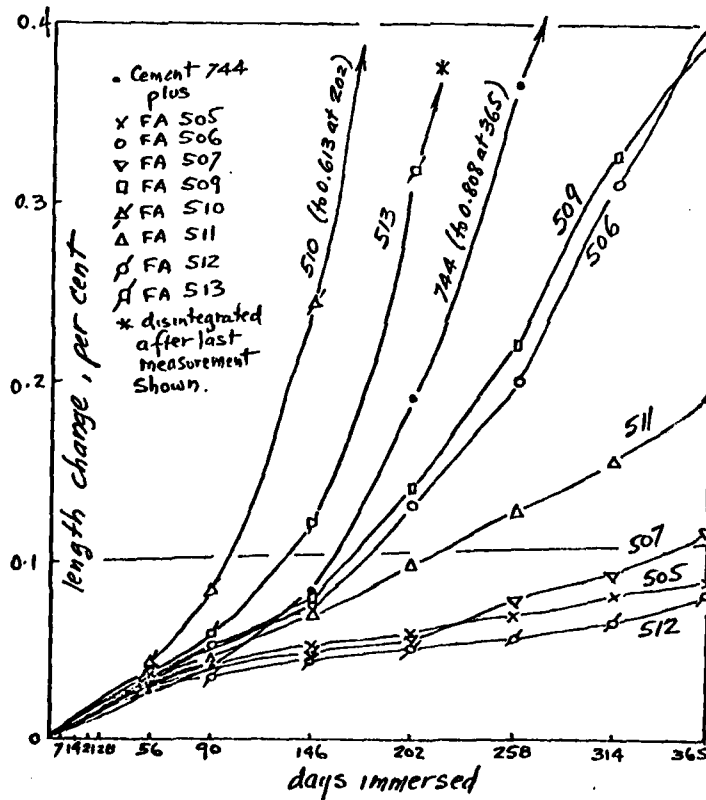


Figure 4

eight fly ashes the effects varied. In contrast to the behavior of these fly ashes with cement 714, here two of them (510 and 513) did significantly increase the sulfate susceptibility of the system; with both of these fly ashes the specimens only survived to 202 days. With all the other six fly ashes the specimens survived to 365 days and, in all cases, with reduced expansions as compared with cement 744 by itself. However only with 505 and 512 was the expansion at 365 days reduced below 0.10 percent, the failure criterion. It is concluded that of the eight fly ashes, the use of two made the sulfate resistance worse, with two others the sulfate expansion was reduced to a possibly tolerable amount, and with the other four expansion was reduced but by not sufficient to provide protection in the test.

Based on the behavior of these ten pozzolans with the three cements (714, 756, 744), they may be ranked from best to worst with regard to their effects on sulfate resistance as follows:

	With Cement			Weighted Average	
	714	756	744		
Best	536	536	536	536	(silica fume)
	518	518	518	518	(volcanic glass)
	512	512	512	512	(subbituminous)
	505	511	505	505	(subbituminous)
	507	507	507	507	(subbituminous)
	513	505	511	511	(bituminous)
	510	513	509	513	(lignite)
	511	509	506	509	(lignite)
	506	510	513	510	(lignite)
	509	506	510	506	(lignite)
Worst					

## CONCLUSIONS

1. It is possible by the use of an X-ray diffractometer to separate cubic  $C_3A$  from solid solutions of  $C_3A$  with alkalies and silica when the solid solutions have crystal structures other than cubic. However without special provisions to improve resolution or the use of monochromatic radiation, the separation of varieties of non-cubic  $C_3A$  is not reliable

unless a step-scanner can be used on the diffractometer or a Guinier camera is available.

2. The cubic and orthorhombic I group following the nomenclature of Regourd, Chromy, et al (4) is probably the next most reliable separation as made with a diffractometer, on the basis of the experimentation by Maki (6) that shows that the partial solid solution in cubic  $C_3A$  passes with increasing substituents into mixed cubic and orthorhombic solid solutions as the substituents increase to a level of 7 percent  $Na_2O$ , modified in commercial portland cements by the  $SiO_2$  content and  $K_2O$  content.

3. We had hoped in this work to provide evidence to support or refute the belief of Regourd, Chromy, et al (4) that cubic  $C_3A$  should be more reactive than any of the solid solutions with  $Na_2O$  which have denser structures. However, our results are not clear regarding this particular question because it developed that bars made using mortars prepared in accordance with ASTM Designation C 109 with constant water-cement ratio and proportions proved to have very different strain capacities, probably as a consequence of the rate of strength gain of the cements even when the  $C_3A$  contents were similar. For example, cement 756, containing the most cubic  $C_3A$  of any of the cements we tested (14.6 percent  $C_3A$  calculated from chemical analysis) in mortar bars exposed in 5 percent  $Na_2SO_4$  solution survived to 90 days and reached an expansion of 0.868 percent; the bars disintegrated before the next reading. When that cement was replaced by 30 percent by volume of each of the eight fly ashes, the expansions were reduced in four cases but failure by disintegration of the bars took place earlier than those made with the cement alone; in one case the bars survived as long as the cement by itself but the expansion was greater. In three other cases the bars containing fly ash survived as long as the bars containing the straight portland cement but disintegrated at lower expansions. In this group, only one fly ash increased the strain capacity. Cement 714 contained 13.1 percent  $C_3A$ , a smaller amount than in cement 756. In C 109 mortar bars it expanded to 0.515 at 56 days and then disintegrated. As compared with cement 756, it had less strain capacity because the bars disintegrated earlier at a

lower expansion. If it were possible to exchange the cubic  $C_3A$  of 756 with the lower cubic and orthorhombic  $C_3A$  of 714, leaving the rest of each cement as it was, would the greater strain capacity of 756 with  $C_3A$  of 714 lead to a larger expansion of that combination before the bars disintegrated? Would the smaller strain capacity of 714 be further decreased by the larger amount of cubic  $C_3A$  from 756? Does strain capacity in sulfate exposure depend on the formation of ettringite and gypsum and the development of tensile strength and creep capacity all pari passu? Does failure by disintegration occur when expansion, strength gain, and creep depart in rate from each other by more than a certain, at present unknown, rate? Cement 744, with 9.4 percent cubic plus orthorhombic  $C_3A$ , less than either 756 or 714, survived in bars exposed in sodium sulfate to 365 days when it had expanded to 0.81 percent. Two fly ashes increased the sulfate susceptibility; one caused earlier failure at lower expansion and the other failure at 365 days at lower expansion. Cement 744 is concluded to have the greatest strain capacity of these three cements, but contained less  $C_3A$ .

4. Because we did not find cements of equal  $C_3A$  content in the cubic, cubic and orthorhombic I, and orthorhombic or tetragonal, or orthorhombic or tetragonal groups, and we did find cements of equal strain capacities in these groups, we can neither confirm nor refute the belief of Regourd, Chromy, et al (4) that cubic  $C_3A$  is more reactive than solid solutions of other crystal forms.

#### BIBLIOGRAPHY

1. A. E. Moore (1966), "Tricalcium Aluminate and Related Phases in Portland Cement," Magazine of Concrete Research, Vol 18, No.55, pp 59-64, English.
2. J. E. Mander, L. D. Adams, and E. E. Larkin (1974), "A Method for the Determination of Some Minor Compounds in Portland Cement and Clinker by X-Ray Diffraction," Cement and Concrete Research, Vol 4, pp 533-544, English.
3. M. A. Shahat (1952), "The Crystal and Molecular Structure of Maleic Acid," Acta Crystallographica, Vol 5, p 763 ff, English.
4. M. Regourd, S. Chromy, L. Hjorth, B. Mortureux, and A. Guinier (1973), "Polymorphisme des Solutions Solides du Sodium dans l'Aluminate Tricalcique," Journal of Applied Crystallography, Vol 6, pp 355-364, French.
5. M. Regourd and A. Guinier (1974), "The Crystal Chemistry of the Constituents of Portland Cement Clinker," preprint of principal paper for the VI International Symposium on the Chemistry of Cement, Moscow, English.
6. I. Maki (1973), "Nature of the Prismatic Dark Interstitial Material in Portland Cement Clinker," Cement and Concrete Research, Vol 3, pp 295-313, English.
7. M. Kristmann (1977), "Portland Cement Clinker: Mineralogical and Chemical Investigations, Part I, Microscopy, X-Ray Fluorescence and X-Ray Diffraction," Cement and Concrete Research, Vol 7, pp 649-658, English.

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References: p. 18.

1. Cements. 2. Mortar (Material). 3. Portland cements. 4. Sulphate resisting. I. United States. Army. Corps of Engineers. II. Series: United States. Waterways Experiment Station, Vicksburg, Miss. Miscellaneous paper ; SL-80-17.  
TA7.W34m no.SL-80-17



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